

Preliminary evaluation of strontium isotope ratios for dating in the subsurface of the Carnarvon Basin, Western Australia

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Manuscript received March 1991; accepted October 1992

Abstract

The results of an experimental programme to evaluate the potential application of Strontium⁸⁷/Strontium⁸⁶ ratios as a dating method in the subsurface of the Carnarvon Basin are presented and discussed. Age estimates from Sr ratios consistent with independent palaeontological dating were obtained from two samples, one from the Middle Jurassic and one from the Late Jurassic. The samples were from relatively deeply buried sequences (1784 and 2923 metres) indicating that diagenesis need not alter strontium ratios in the deep subsurface. The method shows considerable promise for dating in the subsurface of WA and for correlation within Australian basins and to sections abroad, provided suitable sample material is available. Its usefulness in dating for pre-Tertiary sequences is at present limited and further research is required to refine the pre-Tertiary sea-water ⁸⁷Sr/⁸⁶Sr curve.

Introduction

The ratio ⁸⁷Sr/⁸⁶Sr appears to be constant throughout the present oceans and seas of the world. Faure (1986) quotes the present ratio as 0.70906 ± 0.00003 and suggests that the excellent mixing is due to two factors. Strontium has a long residence time of about 5 million years compared to the mixing time of oceans of about 1000 years. Secondly, the concentration of Sr in oceans is high compared with average river water (7.7 micrograms/gram and 0.068 micrograms/gram respectively). The same perfect mixing may be presumed to have occurred throughout Phanerozoic time. However, the ratio is not constant and has varied systematically in the past, reflecting variations in input of strontium to the world's oceans. Animals and plants that build a calcareous skeleton record the strontium ratio of the water in which they exist. By measurement of ⁸⁷Sr/⁸⁶Sr ratios on carbonate material, Burke *et al.* (1982) estimated the variation of the ratio throughout the Phanerozoic. If their best fit curve for the sample spread is accurate (see discussion below), then determining the ratio in fossil fragments in which strontium has not been added or removed during diagenesis provides a method of dating by comparison with the curve, provided the approximate age of the sequence is known. The ratio does not provide an absolute age by itself, as the same ratio can occur more than once within the Phanerozoic (see below).

The aim of this study was to determine if the ratio could be determined in fossil fragments from palynologically dated subsurface samples and if the resulting ratios were in agreement with the relevant part of the curve as presented by Burke *et al.* (1982). We have obtained ⁸⁷Sr/⁸⁶Sr ratios on selected carbonate fossil fragments from Jurassic sequences within the Carnarvon Basin of Western Australia, in order to assess the possible wider application of this technique to the hydrocarbon-rich basins of the Northwest Shelf. The Jurassic was selected for the test as it has considerable economic importance as an oil reservoir and source and is relatively deeply buried in the offshore Carnarvon Basin.

Experimental Procedure

Six samples were collected from three petroleum exploration wells in the Carnarvon Basin (Fig 1). The samples were selected from available cores with fossil fragments visible in parts. Treatment of three of these samples in the laboratory with dilute hydrochloric acid indicated that the fossil fragments were partially or completely dolomitised; these were not analysed further because of the risk that the strontium content was different from the original. Three samples contained fragments of belemnite guard which were still composed of calcite. The strontium content of these fossil fragments was determined by atomic absorption analysis and was found to vary from 5387 to 5096 ppm (Table 1). Veiser (1983) reports that belemnites average about 4000 ppm Sr; these samples were thus judged to retain more or less their original strontium content.

Table 1

⁸⁷Sr/⁸⁶Sr Ratios obtained by analysis. Letters a, b and c refer to repeat analyses performed on material from the same sample. Values are means \pm standard deviation. The error was considered too great to provide a reliable ⁸⁷Sr/⁸⁶Sr ratio for the sample from Bamba-1.

Sample (depth,m)	Sr Concentration (ppm)	⁸⁷ Sr/ ⁸⁶ Sr
NBS 987 (standard)		a: 0.710235 \pm 0.000007 b: 0.710238 \pm 0.000028 c: 0.710231 \pm 0.000014 mean: 0.710235
Rosemary-1 (2923m)	5387	a: 0.707039 \pm 0.000014 b: 0.707065 \pm 0.000007 mean: 0.707052
Anchor-1 (1784m)	5344	a: 0.706941 \pm 0.000014 b: 0.707067 \pm 0.000014 mean: 0.707004
Bamba-1 (2726m)	5096	a: 0.707470 \pm 0.00345 b: 0.707038 \pm 0.00026

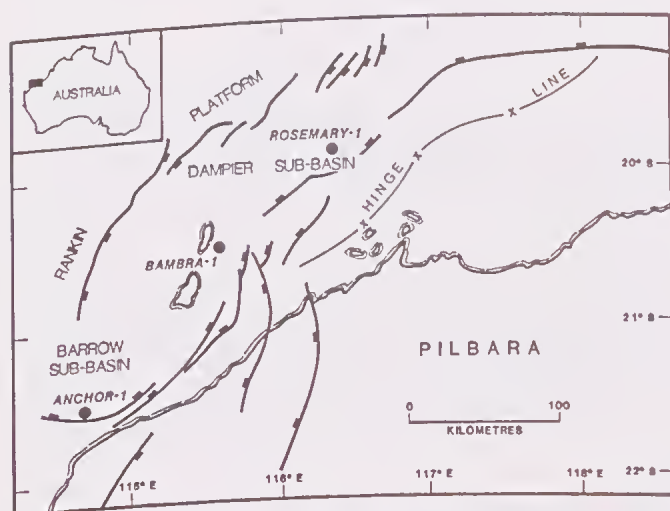


Figure 1 Northwest Shelf of Western Australia: Location of wells from which samples were analysed.

Further samples of the belemnites were coarsely crushed and small fragments with fresh surfaces were hand-picked. Approximately 100 mg of these chips were dissolved overnight in a teflon beaker in 1 ml of 6N HCl. The solution was then evaporated on a hot-plate in a class-100 clean air environment. This procedure was repeated until all the carbonate was dissolved. The solution was then re-evaporated, redissolved in 1N HCl and loaded onto a preconditioned column of Dowex-50 cation exchange resin. After washing with a measured volume of 2N HCl, Sr was isolated in 6N HCl. The solution was then evaporated and approximately 50-100 micrograms of Sr was loaded onto a single Re filament assembly. Sr was analysed on the VG-354 multi-collector mass spectrometer at Curtin University. Recent experience indicates that the best results are obtained using a peak-jumping procedure and a single collector. Multiple analyses of the NBS-987 Sr standard indicate an external precision of ± 0.000016 (1 standard deviation, $n=12$).

Results

Results including analysis of the NBS 987 standard, are presented in Table 1.

The sample from Rosemary-1 (2923m sub-KB) is within an interval dated by palaeontology in the well completion report (Anon 1973) as Callovian to late Bathonian. The Sr ratio from this sample of 0.70705 plots on the 'Burke Curve' (Burke *et al.* 1982) at approximately 170 million years (Fig 2). The Callovian to Bathonian on Van Eysinga's (1975) time scale, used by Burke *et al.* (1982) is between 160 and 167 million years.

The sample from Anchor-1 (1784 metres sub-KB), dated palynologically in the well completion report (Andrejewski 1969) as Tithonian gave a ratio of 0.70700, which plots on the curve at about 145 million years. The Tithonian on Van Eysinga's scale is between 141 and 145 million years.

The results from Anchor-1 and Rosemary-1 are thus in good agreement with the palaeontological data.

The sample from Bamba-1 (2725.7m sub-KB) did not produce values within an acceptable error.

Discussion

These results indicate that the Sr ratio method has considerable promise as a dating and correlation tool in the subsurface of Western Australia. There was close agreement between dating by fossils and by Sr ratios in two out of the three samples studied. However, the results can only be considered a preliminary test. The method can provide an absolute value or series of values, provided suitable sample material is available. The method only requires small quantities of well-preserved carbonate material which can be in the form of fossil fragments. This is a considerable advantage in subsurface analysis. However, as an dating technique, there are still considerable limitations to its use. The approximate age of the sample must be known. The ratio 0.7070 for example occurs four times in the Jurassic and Permian on the 'best fit' Burke curve (Fig 2). The 'best fit curve' has been determined from a

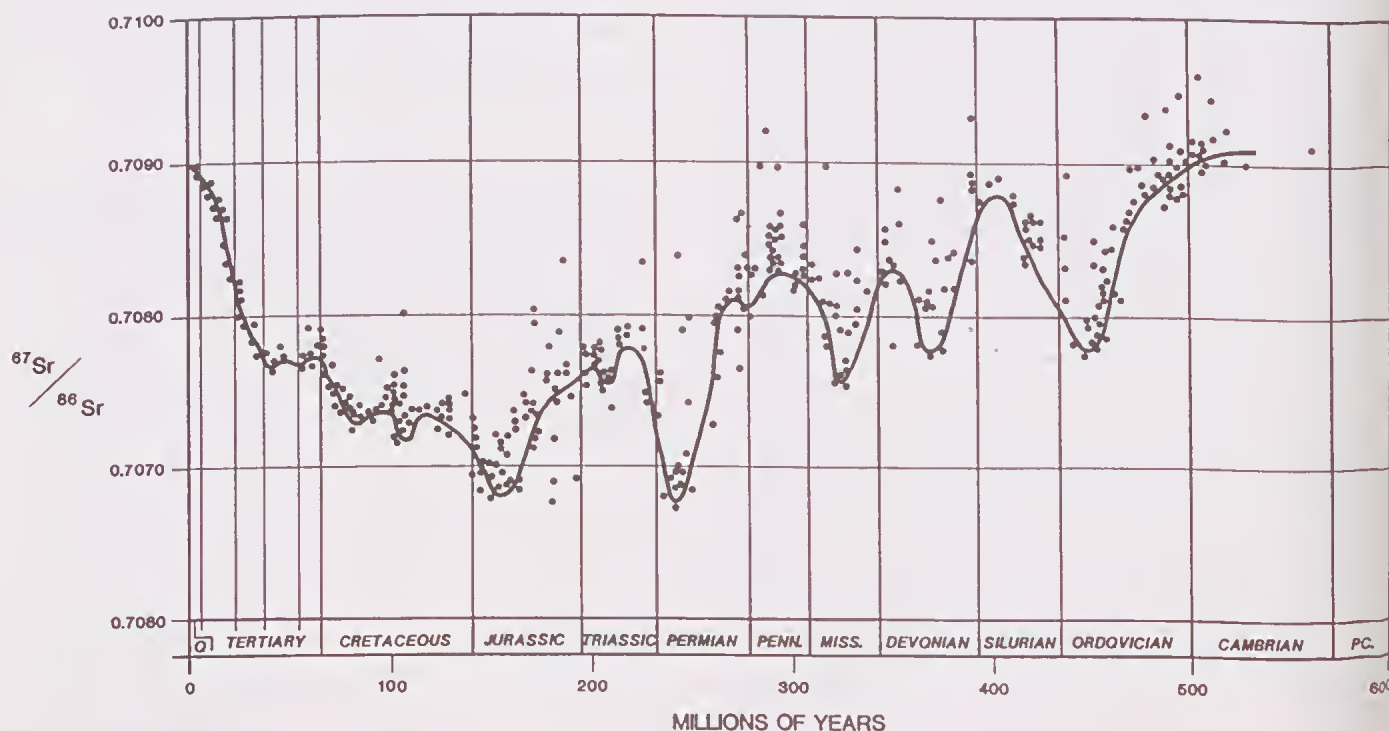


Figure 2 The 'Burke Curve' of the variation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with time in the world ocean, based on the analysis of 744 samples. The line represents the best-fit curve through the data; modified from Burke *et al.* (1982).

wide spread of results in the pre-Tertiary. The spread increases with increasing age. Burke *et al.* (1982) suggest four possible reasons for this:

1. The strontium ratios of the samples are in some cases not representative of the world ocean.
2. Small but relatively rapid fluctuations may have occurred at times in the past, and thus the curve may be more variable than shown.
3. Errors may have occurred in the palaeontological dating of samples analysed for constructing the curve.
4. Diagenesis has altered the Sr ratios in the samples since deposition.

The extent of the potential problem with diagenesis can be minimised by analysing samples composed of low-magnesian calcite, diagenetically the most stable form of CaCO_3 . Belemnite fragments are thus suitable and possess the added potential advantage that they were an open-ocean nektonic faunal element, and may be expected to have retained an open ocean strontium signature, minimising potential problems with nearshore variations in strontium ratio. Excluding samples that appear to contain an altered strontium content should also improve the accuracy. Burke *et al.* (1982) found they were able to define a better curve by ignoring samples with a Sr content lower than 200 ppm, and samples with a high insoluble residue.

The problem that samples may not be representative of the world ocean signature may be particularly acute at times of warm global climate. Today, the world ocean is well mixed, reflecting the vigorous circulation driven by the cold polar areas. At times of widespread oceanic anoxia, in the Mesozoic, the ocean was possibly not well mixed and a variation in strontium ratios, particularly in isolated embayments or broad shallow seas could have occurred. It is interesting to note that the widest spread of samples from the best fit curve in the Cretaceous occurs at around 100 million years, coincident with the maximum development of the Aptian-Albian oceanic anoxic event (itself the best developed and longest lasting oceanic anoxic event recognised in the Cretaceous (Jenkyns 1986)).

A fundamental problem with the 'Burke curve' is raised by the question of accuracy of palaeontological dating of samples which form the basis of the curve. At present, the magnitude of the error cannot be determined because *where* the error occurs is unknown—is the age wrong or is the strontium ratio wrong or are they both wrong? The curve will only become really useful if accurate ratios can be determined for individual stages at their type sections where the ages of zones and substages are known by definition. A Phanerozoic curve could then be constructed from the determination of individual type sections. Such determinations will also show if there have been short term fluctuations in the $^{87}\text{Sr}/^{86}\text{Sr}$ curve which are not apparent in the general curve.

Finally, the curve may be improved by careful sampling of single faunal elements, preferably of low magnesium calcite rather than bulk carbonate samples. It is not clear if Burke *et al.* (1982) used bulk rock samples or individual faunal elements, but other studies, such as Faure *et al.* (1978) and Tremba *et al.* (1975) were based on analysis of bulk samples and their results are not particularly consistent with the 'Burke Curve'. Complex diagenesis in carbonates is the norm, and it is easy to envisage different

elements that make up the rock attaining different strontium contents during diagenesis. Consistent, repeatable results would not always be expected therefore from bulk sample analysis.

The strontium ratio method of dating and correlation shows considerable promise for use in subsurface studies, provided material which retains the original signature of the Sr ratio is available for analysis. There are a number of problems to be overcome before the world curve is accurate or unambiguous enough for widespread use. Determinations of the variation of the ratios in stage type sections needs to be undertaken. The method will never replace dating by other means, particularly palaeontological dating, because very few $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are unique to one time. The ratio 0.7080, for example, occurs 7 times in the Palaeozoic and once in the Tertiary. The method is also of no or limited use around points of rapid change from an increasing to a decreasing ratio. Although the method is only really useful in the Tertiary, where control is good and the curve well and unambiguously defined, it will find wider application in older sequences as the sea-water Sr isotopic variation curve becomes better defined. The method is relatively quick and requires very little sample material. It can be performed on fossil fragments and has particular application in stratigraphic correlation between boreholes.

Acknowledgements: We wish to thank the Geological Survey of Western Australia for providing access to the sample material. The costs of undertaking this pilot project were met partially from funds provided by Western Mining Corporation Petroleum Division, and this support is gratefully acknowledged. We thank Susan Clark for drafting and Wendy Scott for word processing assistance.

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